

10/529764<sup>529,764</sup>

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
8 April 2004 (08.04.2004)

PCT

(10) International Publication Number  
**WO 2004/029116 A1**

(51) International Patent Classification<sup>7</sup>: **C08F 292/00,**  
283/01

[ZA/ZA]; c/o 10 Frederick Cooper Drive, Fatoria, Gauteng, 1739 Krugersdorp (ZA).

(21) International Application Number:  
PCT/ZA2003/000140

(74) Agent: **MORRISON FORSTER INC;** FMI House, Gleneagles Park, Flanders Drive, Mount Edgecombe, Kwa Zulu Natal, P O Box 2004, Mount Edgecombe, Kwa Zulu Natal, 4300 Durban (ZA).

(22) International Filing Date:  
23 September 2003 (23.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
02/7813 30 September 2002 (30.09.2002) ZA

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for all designated States except US*): **BARLOWORLD PLASCON S.A. (PTY) LIMITED** [ZA/ZA]; 10 Frederick Cooper Drive, Fatoria, Gauteng, 1739 Krugersdorp (ZA).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors: **ENGELBRECHT, John, Francis;** c/o Frederick Cooper Drive, Fatoria, Gauteng, 1739 Krugersdorp (ZA). **DE WET-ROOS, Deon;** c/o 10 Frederick Cooper Drive, Fatoria, Gauteng, 1739 Krugersdorp (ZA). **SMIT, Albertus, Christiaan;** c/o 10 Frederick Cooper Drive, Fatoria, Gauteng, 1739 Krugersdorp (ZA).

**Published:**

— with international search report

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **COORAY, Boyd**

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **VESICULATED POLYMER PARTICLES**

(57) Abstract: Vesiculated polymer particles and a method of manufacture thereof, are suitable for the beneficial replacement of titanium dioxide pigments and extenders amongst others, and have improved opacity, whiteness, scrub resistance and water resistance due. The manufacturing process exhibits effective control of particle size and particle size distribution.

WO 2004/029116 A1

**VESICULATED POLYMER PARTICLES****TECHNICAL FIELD OF THE INVENTION**

This invention relates to vesiculated polymer particles and a method of manufacture thereof, with particular relevance to their use in coating compositions.

**5 BACKGROUND ART**

The morphology of cross-linked multi- vesiculated polyester particles described in prior art consist of largely spherical hollow particles with multiple air voids in the dry state. These particles re-absorb water in paints and coatings, are difficult to manufacture and their particle size control is limited to processing variables such as temperature, speed of  
10 agitation and process time.

It is an object of this invention to provide cross-linked polyester particles whose morphology is largely spherical with multiple air voids that hinder the re-entry and re-absorption of water when the cross-linked particles are dry.

It is a further object of the invention to provide a conversion process of the raw materials  
15 composition which permits cross-linked particle size and distribution control through process variables such as temperature, rate of agitation and processing time as well through the concentration of modifying co-monomer in the raw material composition and the optimization of the process stage for adding this co-monomer to the said composition.

It is yet a further object of this invention to provide a vesiculated polymer particle which  
20 may be used in paint and coatings formulations for the beneficial replacement of titanium dioxide pigments, expensive extenders, emulsion polymers, open time modifiers such as glycols and humectants with simultaneous achievement of improved opacity, whiteness, scrub resistance, water resistance and special faux finish effects.

## ***DISCLOSURE OF THE INVENTION***

According to the invention, vesiculated polymer particles include particulate solids and have associated with the surfaces thereof, long chain aliphatic chemical groups and/or sterically hindered, branched chained chemical groups.

- 5 In the one form of the invention, the chemical groups are hydrophobic and comprise organic compounds with at least one polymerisable carbon - carbon double bond with linear, branched or cyclic moieties having at least four carbon atoms, including but not limited to :

Glycidyl methacrylate; Octadecene; Lauryl methacrylate; Ethylene glycol di methacrylate  
10 (EGDMA); Cyclohexene; Acrylated castor oil; Acrylated ricinoleic acid; Methacrylated ricinoleic acid; Hydroxy-ethyl acrylate; Soya Bean Oil; Unsaturated fatty acids, e.g. Oleic acid, tallow fatty acid; Unsaturated fatty alcohols, e.g. Oleyl alcohol, pentadeca-12-ene-1-ol.; Oleamide; Triglycerides, e.g. tall oil, ting oil; Ethylenic unsaturated urethanes; Acrylic unsaturated urethanes; Air drying short oil alkyds; Alkyl  
15 and Aryl Esters of maleic anhydride, singly or in combination.

In this description, the term associated may refer to groups included in the polymer particles or applied to the surface or portions of the surface thereof.

- According to a second aspect of the invention, a raw material composition for manufacture of vesiculated particles includes a carboxylic acid functional, free-radical polymerizable  
20 polyester resin, a co-reactive diluent monomer and a modifying co-monomer, the modifying co-monomer including at least one polymerisable carbon - carbon double bond with linear, branched or cyclic moieties having at least four carbon atoms, including but not limited to :

Glycidyl methacrylate; Octadecene; Lauryl methacrylate; Ethylene glycol di methacrylate  
25 (EGDMA); Cyclohexene; Acrylated castor oil; Acrylated ricinoleic acid; Methacrylated ricinoleic acid; Hydroxy-ethyl acrylate; Soya Bean Oil; Unsaturated fatty acids, e.g. Oleic

acid, tallow fatty acid; Unsaturated fatty alcohols, e.g. Oleyl alcohol, pentadeca-12-ene-1-ol.; Oleamide; Triglycerides, e.g. tall oil, tinging oil; Ethylenic unsaturated urethanes; Acrylic unsaturated urethanes; Air drying short oil alkyds; Alkyl and Aryl Esters of maleic anhydride, singly or in combination.

- 5 The modifying co-monomer may comprise between 3 and 20% by mass of the added or reactive diluent monomer, and preferably comprises between 5 and 9% by mass of the added diluent monomer. This excludes the diluent monomer present in the polyester resin.

Suitable diluent co-monomers comprise ethylenic, acrylic and methacrylic functional monomers for example styrene, butyl acrylate, methyl methacrylate and preferably

10 styrene.

In one form, the polyester resin composition comprises :

Propylene glycol	30,35%
Phthalic anhydride	12.96%
Maleic anhydride	25.75%
15 Styrene	30.75%
Inhibitor (10% solution)	0.18%
TOTAL	100,00

According to a third aspect of the invention, a method of manufacture of the vesiculated particles includes the steps of

- 20       -     pre-dispersing pigment particles in a polyester;
- dissolving the pre-dispersed pigment-polyester in a suitable monomer in the presence of a water-soluble base;
- forming a stable emulsion of droplets of solution of the pre-dispersed pigment-polyester and monomer (oil phase) in water;
- 25       -     adding a hydrophobic monomer
- and polymerising the polyester and co-polymerisable monomer thereby producing granules of opaque, cross-linked vesiculated particles as a

dispersion in water, the particles including hydrophobic groups associated with their surfaces.

In one form, the base may comprise a polyamine, for example diethylenetriamine.

5 Particles of various sizes may be manufactured using different mixers with different mixing intensity when emulsifying the polyester in water. In one form of the invention, suitably designed equipment controlling pressure, temperature, and residence time, for example homogenisers, may be used. Chemical control of particle size and particle size distribution is also effected by the introduction of long chain aliphats or sterically hindered, branched, chained co-monomers.

- 10 As most of these monomers or macro-monomers when incorporated into vesiculated polymer particles coarsen the average particle size, it was found preferable to add it at a later stage during emulsification of the organic phase in the water phase. This minimised the effect on particle size. The coarser particle size versions can however be used to impart special effects in paint *e.g.* texture.
- 15 The modified vesiculated polymer particles when incorporated into paint systems had the effect of improving water resistance, abrasion resistance, whiteness and opacity.

### **EXAMPLES**

The following examples are intended to illustrate the invention, but are not presented as limitations on the scope of the invention.

20 **Example 1**

The following vesiculated polymer particles were synthesized as per prior art.

	Parts by Weight
<b><u>Stage 1</u></b>	
Polyester	14,99
Titanium Dioxide	0,86
Styrene	6,54
Diethylene Triamine	0,21
<b><u>Stage 2</u></b>	
Polyvinyl alcohol solution (10%)	13,28
Hydroxy Ethyl cellulose solution (2.5%)	10,45
Water	52,92
Diethylene Triamene	0,06
<b><u>Stage 3</u></b>	
Water	0,21
Ferrous Sulphate	0,01
Cumene Hydroperoxide	0,12
<b><u>Stage 4</u></b>	
Bacteriacide	0,35
	100,00

### **Procedure**

1. The Titanium Dioxide is dispersed in the polyester at high speed in a high shear mixture.
- 5 2. Styrene and Diethylene Triamine is added to 1) above at low speed.
3. Stage 2 is prepared in a separate vessel at low speed.
4. Stage 1 (organic phase) is added to Stage 2 at high speed on a high shear mixture and stirred until the desired particle size of the organic phase is obtained.
5. Stage 3 is then added at low shear by firstly pre-mixing the Ferrous Sulphate and water
- 10 and then added. This is followed by adding the Cumene Hydroperoxide.
6. The stirrer is stopped and the product is left undisturbed to cure overnight.
7. The vesiculated particles are then stirred until homogenous and a suitable bacteriacide is added.

A fluid white dispersion of cross-linked polymer particles is obtained in water which on drying forms non-film forming particles with multiple air voids present.

Average particle size will vary depending on the stirring intensity used when adding Stage 1 to Stage 2.

**Example 2**

As per Example 1 but 0,1% of the Styrene was replaced with Lauryl Methacrylate.  
Stirring conditions as per Example 1.

**Example 3**

- 5 As per Example 1 but 3% of the Styrene was replaced with Lauryl Methacrylate. Stirring conditions as per Example 1.

**Example 4**

As per Example 1 but 5% of the Styrene was replaced with Lauryl Methacrylate. Stirring conditions as per Example 1.

10 **Example 5**

As per Example 1 but 7% of the Styrene was replaced with Lauryl Methacrylate. Stirring conditions as per Example 1.

**Example 6**

- 15 As per Example 1 but 9% of the Styrene was replaced with Lauryl Methacrylate. Stirring conditions as per Example 1.

**Example 7**

As per Example 1 but 20% of the Styrene was replaced with Lauryl Methacrylate. Stirring conditions as per Example 1.

**Example 8**

- 20 The vesiculated particles produced in the above examples 1 to 7 were measured for the following properties:

1. Total solids content using a Mettler HR73 halogen moisture analyzer.
2. Viscosity using a Brookfield LVT viscometer.
3. pH using a Metrohm 744 pH meter.
- 25 4. Specific gravity using a Sheen 100cc "weight per gallon" cup.

5. Opacity using Leneta form 2A opacity charts and Sheen micropac reflectometer.
6. Whiteness using BYK-Gardner color-view spectrophotometer.
7. Average particle size using a scanning electron microscope (Topcon & Scion image analysis software).

5 Results as follows:

Vesiculated Particles Manufactured on Variable Shear Cowles Mixer							
LMA %	Solids, %	Viscosity, cps	pH	S.G.	Opacity	Whiteness	Average Particle Size, microns
0	23.50	800	6.78	1.043	0.93	94.0	5.6
0.1	23.80	610	6.66	1.044	0.96	96.7	6.1
3	23.90	1200	6.50	1.044	0.96	96.1	6.9
5	23.63	1250	6.55	1.046	0.95	96.4	7.5
7	23.7	3720	6.74	1.042	0.96	97.0	8.3
9	23.46	3900	6.75	1.044	0.95	95.4	16.0
20	23.67	14800	6.73	1.033	0.88	94.5	36.5

The improvement in opacity and whiteness is clearly illustrated as well as the effect of increase particle size.

#### Example 9

- 10 The vesiculated polymer particles from Example 1 to 7 were formulated into the following mixture to produce water based emulsion paint:

RAW MATERIAL		PARTS BY WEIGHT
Vesiculated Particles		77.5
Styrene Acrylic Emulsion Polymer		9.7
15	Coalescent	1.1
Ammonia (Diluted 1:1 with water)		1
Titanium Dioxide Aqueous Dispersion		9.7
Thickener		1

- The paints obtained by using the vesiculated particles from Examples 1 to 7 in this Example were tested for wet scrub (abrasion) resistance and the following results recorded:
- 20



- |      |  |   |             |
|------|--|---|-------------|
| 1.   | Paint using Vesiculated Particles from Example 1 | = | 20 cycles   |
| 2.   | Paint using Vesiculated Particles from Example 2 | = | 120 cycles  |
| 3.   | Paint using Vesiculated Particles from Example 3 | = | 500 cycles  |
| 4.   | Paint using Vesiculated Particles from Example 4 | = | 1100 cycles |
| 5 5. | Paint using Vesiculated Particles from Example 5 | = | 1500 cycles |
| 6.   | Paint using Vesiculated Particles from Example 6 | = | 900 cycles  |
| 7.   | Paint using Vesiculated Particles from Example 7 | = | 600 cycles  |

The higher wet scrub cycles indicate better scrub and abrasion resistance in the final paint. The results confirm the improvements in water and scrub resistance obtained by using the compositions of this invention in paints and coatings.

#### Example 10

Repeat of Example 4 but using Octadecene instead of Lauryl Methacrylate. Stirring conditions as per Example 1.

#### Example 11

- 15 Repeat of Example 4 but using Acrylated Methyl Ricinoleate instead of Lauryl Methacrylate. Stirring conditions as per Example 1.

#### Example 12

Repeat of Example 4 but using Methacrylated Ricinoleate instead of Lauryl Methacrylate. Stirring conditions as per Example 1.

#### 20 Example 13

The vesiculated polymer particles from Examples 10, 11 and 12 were measured for properties as above in Example 8.

Results as follows:

<b>Vesiculated Particles Manufactured on Variable Shear Cowles Mixer</b>							
<b>Example</b>	<b>Solids, %</b>	<b>Viscosity, cps</b>	<b>pH</b>	<b>S.G.</b>	<b>Opacity</b>	<b>Whiteness</b>	<b>Average Particle Size, microns</b>
<b>10</b>	23.39	10000	6.56	1.045	0.95	95.0	17
<b>11</b>	23.48	1800	6.72	1.043	0.96	95.4	9
<b>12</b>	23.50	1900	6.47	1.045	0.96	95.2	9

#### **Example 14**

The vesiculated polymer particles from Example 10, 11 and 12 were formulated into water-based paint as per Example 9 and tested for wet scrub (abrasion) resistance.

- 5 1. Paint using vesiculated particles from Example 1 = 20 cycles.
2. Paint using vesiculated particles from Example 10 = 500 cycles.
3. Paint using vesiculated particles from Example 11 = 1000 cycles.
4. Paint using vesiculated particles from Example 12 = 1200 cycles.

The results confirm the improvements in water and scrub resistance obtained by using the

10 compositions of this invention in paints and coatings.

#### **Example 15**

The water resistance and whiteness of paint containing:

Vesiculated particles synthesized using prior art technology (Example 1).

Vesiculated particles synthesized using the present patent technology (Example 4).

- 15 were compared. The paint is of medium quality and suitable for both interior and exterior use.

The following are the results obtained.

<b>Paint Vesiculated Particles from</b>	<b>A (Example 1)</b>	<b>B (Example 4)</b>
<b>Water resistance</b>		
• Water droplet method <sup>(1)</sup>	5 min	10 min.
• Wet abrasion resistance <sup>(2)</sup>	1280 cycles	2198 cycles
Colour D10° (against Std) <sup>(3)</sup>		
L	- 0.28 D	- 0,51 D
A	- 0.06 G	- 0.10G
B	1.09 Y	0.43 Y
DE CMC	1.41	0.63

- (1) Water resistance by this method is done by subjecting a paint film which has been dried at ambient temperature for 24 hours to water droplets on the surface of the paint. The time taken for blistering or softening of the paint in contact with the water droplet is recorded. The longer the time the better the water resistance. The test is stopped after 10 minutes.
- (2) Wet abrasion resistance is done by the attached method. The higher the number of cycles, the better the wet abrasion resistance.
- (3) Colour is measured on a colour computer and compared to the paint containing vesiculated particles from example 1.
- The L value if positive indicates lightness difference and if negative the darkness difference. Paint B is slightly darker than Paint A.
- The A value if positive indicates redness difference and if negative, the greenness difference. Paint B is very slightly greener than Paint A.
- The B value if positive indicates the yellowness difference and if negative, the blueness difference. Paint B is less yellow than Paint A and thus whiter.
- The DE CMC is the overall difference in colour. Paint B has less overall colour change than Paint A.

### Example 16

- 20 Vesiculated particles (i.e. Example 1 and Example 4) were formulated into the following waterbased paints:
- Medium quality interior/exterior paint.
  - High quality interior matt paint
  - Effects paint
- 25 The properties of the paints were evaluated.
- Listed below are the paint formulations and the test results:

### Example 17

Vesiculated particles were synthesized as per Example 1 and Example 4.

The vesiculated particles were applied to a black and white opacity chart by means of a 200mm drawdown bar.

The opacity (i.e. obliterating power) was measured over the black and over the white portions of the opacity chart by means of a reflectometer. The resultant reflectance measurement over the white is divided into the reflectance measurement over the black.

Results as follows:

	Example 1	Example 4
Opacity	0,93	0,95

The higher the figure the greater the obliterating power of the vesiculated bead.

### High Quality Matt Interior/Exterior Paint

	Paint A	Paint B
Water	28.11	28.11
Dispersant	0.24	0.24
Titanium Dioxide	7.90	7.90
Calcium Carbonate (2 micron)	21.82	21.82
Calcium Carbonate (5 micron)	8.11	8.11
Propylene Glycol	1.02	1.02
Anionic Surfactant	0.09	0.09
Defoamer	0.31	0.31
Hydroxy Ethyl Cellulose	0.33	0.33
Ammonia	0.11	0.11
Styrene/Acrylic Emulsion (50% solids)	17.20	17.20
Coalescent	1.66	1.66
Bacteriacide	0.21	0.21
Vesiculated Particles (Example 1)	12.91	-
Vesiculated Particles (Example 2)	-	12.91
<b>TOTAL</b>	<b>100.0</b>	<b>100.0</b>

### RESULTS

	Paint A	Paint B
Water resistance		
• Water droplet method	8	10
• Wet abrasion resistance	>10,000	>10,000
Opacity	0.88	0.92
Whiteness <sup>(1)</sup>	79.57	81.06

**Note:** Paint B is more water resistant, higher opacity and whiter than Paint A.

- (1) Whiteness is measured on a colour computer. The higher the figure the whiter the paint.

### **High Quality Matt Interior Paint**

	Paint A	Paint B
1. Titanium Dioxide dispersion	21.32	21.32
2. Talc dispersion	19.07	19.07
3. Thickener	0.29	0.29
4. Water	2.02	2.02
5. Ammonia	0.24	0.24
6. Propylene Glycol	0.77	0.77
7. Coalescent	1.345	1.345
8. Defoamer	0.25	0.25
9. Dispersant	0.19	0.19
10. Bacteriacide	0.10	0.10
11. Pure acrylic Emulsion (48% solids)	39.55	39.55
12. Thickener (for low shear)	0.15	0.15
13. Thickener (for high shear)	0.29	0.29
14. Water	2.95	2.95
15. Vesiculated particles <sup>(1)</sup>	11.51	-
16. Vesiculated particles <sup>(2)</sup>	-	11.51
<b>TOTAL</b>	<b>100.0</b>	<b>100.0</b>

## **5 RESULTS**

	Paint A	Paint B
Water resistance		
• Water droplet method	8	10
• Wet abrasion resistance	>10,000	>10,000
Opacity	92.8	95.1
Whiteness	78.23	82.14

**Note:** Paint B is more water resistant, higher opacity and whiter than Paint A.

- (1) Vesiculated particles were manufactured to the particle size as per Example 1 and at 25 micron average particle size by adjusting the rate of agitation
- 10 (2) Vesiculated particles were manufactured to the particle size as per Example 4 and at 25 micron average particle size

**Effects Paint**

	<b>Parts by Weight</b>	
	<b>Paint A</b>	<b>Paint B</b>
1. Water	6.07	6.07
2. Propylene Glycol	1.79	1.79
3. Dispersant	0.11	0.11
4. Surfactant	0.18	0.18
5. Defoamer	0.09	0.09
6. Bacteriacide	0.05	0.05
7. Ammonia	0.10	0.10
8. Hydroxy Ethyl Cellulose	0.05	0.05
9. Pure Acrylic Emulsion (48% solids)	47.04	47.04
10. Coalescent	2.09	2.09
11. Vesiculated particles <sup>(1)</sup>	39.16	-
12. Vesiculated particles <sup>(2)</sup>	-	39.16
13. Thickener	1.23	1.23
14. Water	0.82	0.82
15. Colour tinter(s)	1.22	1.22
<b>TOTAL</b>	<b>100.0</b>	<b>100.0</b>

**RESULTS**

	<b>Paint A</b>	<b>Paint B</b>
5 Suede Effect <sup>(3)</sup>	No	Yes

(1) Vesiculated particles were manufactured to the particle size as per Example 1 and at 25 micron average particle size by adjusting the rate of agitation

(2) Vesiculated particles were manufactured to the particle size as per Example 4 and at 25 micron average particle size

10 (3) The Suede Effect is an effect imparted to a paint to give a colour texture effect.

Paint B has superior Suede Effect than Paint A as vesiculated bead is more prominent on the surface due to low water absorption.

**CLAIMS:**

1. Vesiculated polymer particles characterised in that they include particulate solids and have associated with the surfaces thereof, long chain aliphatic chemical groups and/or sterically hindered, branched chained chemical groups.
- 5 2. Vesiculated polymer particles according to claim 1 characterised in that the chemical groups are hydrophobic.
3. Vesiculated polymer particles according to claim 1 or claims characterised in that the chemical groups include at least one polymerisable carbon - carbon double bond with linear, branched or cyclic moieties having at least four carbon atoms, including but not  
10 limited to :  
Glycidyl methacrylate; Octadecene; Lauryl methacrylate; Ethylene glycol di methacrylate (EGDMA); Cyclohexene; Acrylated castor oil; Acrylated ricinoleic acid; Methacrylated ricinoleic acid; Hydroxy-ethyl acrylate; Soya Bean Oil; Unsaturated fatty acids, e.g. Oleic acid, tallow fatty acid; Unsaturated fatty alcohols, e.g. Oleyl alcohol,  
15 pentadeca-12-ene-1-ol.; Oleamide; Triglycerides, e.g. tall oil, ting oil; Ethylenic unsaturated urethanes; Acrylic unsaturated urethanes; Air drying short oil alkyds; Alkyl and Aryl Esters of maleic anhydride, singly or in combination.
4. A raw material composition for manufacture of vesiculated particles according to any of the above claims characterised in that it includes a carboxylic acid functional,  
20 free-radical polymerisable polyester resin, a co-reactive diluent monomer and a modifying co-monomer, the modifying co-monomer including at least one polymerisable carbon - carbon double bond with linear, branched or cyclic moieties having at least four carbon atoms, including but not limited to :

Glycidyl methacrylate; Octadecene; Lauryl methacrylate; Ethylene glycol di methacrylate (EGDMA); Cyclohexene; Acrylated castor oil; Acrylated ricinoleic acid; Methacrylated ricinoleic acid; Hydroxy-ethyl acrylate; Soya Bean Oil; Unsaturated fatty acids, e.g. Oleic acid, tallow fatty acid; Unsaturated fatty alcohols, e.g. Oleyl alcohol, pentadeca-12-ene-1-ol.; Oleamide; Triglycerides, e.g. tall oil, ting oil; Ethylenic unsaturated urethanes; Acrylic unsaturated urethanes; Air drying short oil alkyds; Alkyl and Aryl Esters of maleic anhydride, singly or in combination.

- 5 5. Vesiculated polymer particles according to claim 4 characterised in that the modifying co-monomer comprises 3 to 20% by mass of the reactive diluent monomer.
- 10 6. Vesiculated polymer particles according to claim 5 characterised in that the modifying co-monomer comprises 5 to 9% by mass of the reactive diluent monomer.
7. Vesiculated polymer particles according to claims 4 to 6 characterised in that the diluent monomer comprises ethylenic, acrylic and methacrylic functional monomers, singly or in combination.
- 15 8. Vesiculated polymer particles according to claim 7 characterised in that the diluent co-monomers comprise styrene, butyl acrylate, methyl methacrylate, singly or in combination.
9. Vesiculated polymer particles according to claims 4 to 8 characterised in that the polyester resin composition comprises by mass %, propylene glycol 30,35%, phthalic  
20 anhydride 12,96%, maleic anhydride 25,75%, styrene 30,75%, inhibitor (10% solution) 0.18%.



10. A method of manufacture of vesiculated particles according to claims 1 to 3 characterised in that it includes the steps of :

- pre-dispersing pigment particles in a polyester;
- dissolving the pre-dispersed pigment-polyester in a suitable monomer in the presence of a water-soluble base;
- forming a stable emulsion of droplets of solution of the pre-dispersed pigment-polyester and monomer (oil phase) in water;
- adding a hydrophobic monomer and polymerising the polyester and co-polymerisable monomer thereby producing granules of opaque, cross-linked vesiculated particles as a dispersion in water, the particles including hydrophobic groups associated with their surfaces.

11. A method of manufacture of vesiculated particles according to claim 10 characterised in that the base comprises a polyamine.

12. A method of manufacture of vesiculated particles according to claim 11 characterised in that the base comprises diethylenetriamine.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/LA 03/00140

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F292/00 C08F283/01

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F C08K C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 81 01711 A (DULUX AUSTRALIA LTD) 25 June 1981 (1981-06-25) page 7, line 17 -page 8, line 5; claims; examples 1,5	1-12
X	US 5 972 809 A (MARTIN ROXALANA L ET AL) 26 October 1999 (1999-10-26) column 6; claim 1; example II	1-8
A	EP 0 307 139 A (CANADIAN IND) 15 March 1989 (1989-03-15) claim 1; examples	1-12
A	EP 0 622 402 A (ICI PLC) 2 November 1994 (1994-11-02) examples	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

14 November 2003

Date of mailing of the international search report

27/11/2003

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Wirth, M

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC 03/00140

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 8101711	A	25-06-1981	AT 8645 T	15-08-1984
			AU 533959 B2	22-12-1983
			AU 6462280 A	24-09-1981
			WO 8101711 A1	25-06-1981
			BE 886501 A1	01-04-1981
			BR 8008969 A	20-10-1981
			CA 1139048 A1	04-01-1983
			DE 3068731 D1	30-08-1984
			DK 521380 A ,B,	08-06-1981
			EP 0041508 A1	16-12-1981
			ES 8200914 A1	16-02-1982
			IE 50478 B1	30-04-1986
			IT 1141122 B	01-10-1986
			JP 3054127 B	19-08-1991
			JP 56501731 T	26-11-1981
			NZ 195624 A	21-12-1982
			US 4321332 A	23-03-1982
			ZA 8007354 A	28-07-1982
			ZW 29780 A1	30-06-1982
US 5972809	A	26-10-1999	US 5830928 A	03-11-1998
			WO 9730097 A1	21-08-1997
EP 0307139	A	15-03-1989	US 4808633 A	28-02-1989
			AT 103942 T	15-04-1994
			AU 606443 B2	07-02-1991
			AU 2035288 A	09-03-1989
			BR 8804593 A	11-04-1989
			CA 1302646 C	02-06-1992
			DE 3888902 D1	11-05-1994
			DE 3888902 T2	21-07-1994
			EP 0307139 A2	15-03-1989
			FI 884136 A	09-03-1989
			JP 1103656 A	20-04-1989
			NO 883971 A	09-03-1989
			NZ 225558 A	27-03-1990
			US 4826881 A	02-05-1989
			US 4917765 A	17-04-1990
			ZA 8805869 A	30-05-1989
EP 0622402	A	02-11-1994	AU 670363 B2	11-07-1996
			AU 6068494 A	03-11-1994
			CA 2121382 A1	30-10-1994
			CN 1094414 A ,B	02-11-1994
			EP 0622402 A1	02-11-1994
			US 5470887 A	28-11-1995
			ZA 9402650 A	18-10-1995